METAL DERIVATIVES OF COMPOUNDS RELATED TO THE AZO DYES

PART I. THE NATURE OF THE COORDINATION BOND BETWEEN THE AZO GROUP AND THE METAL ATOM IN LAKES OF AZO DYES

PART II. THE TENDENCIES OF VARIOUS METALLIC ELEMENTS TO FORM LAKES WITH AZO DYES

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B.S., Tulane University, 1944
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AN ABSTRACT OF A THESIS

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ACKNOWLEDGMENT

The author wishes to express his sincere appreciation to Professor John C. Bailar, Jr., for his encouragement and advice in directing this research.

He is also grateful to Dr. Scott Anderson, to members of the faculty, and to fellow students for numerous suggestions.

The author wishes to thank the General Aniline and Film Corporation for the research assistantship which was provided for this study.

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METAL DERIVATIVES OF COMPOUNDS RELATED TO THE AZO DYES

Part I. The Nature of the Coordination Bond between the Azo Group and the Metal Atom in Lakes of Azo Dyes

It has been shown, especially by Drew and coworkers (1), that many "lakes," *i.e.*, metal derivatives, of azo dyes are coordination compounds. The azo compound acts as a polydentate group in which coordination to the central metal atom occurs through the azo group and through one or two active functional groups located *ortho-* to the azo group. In most cases, each of these functional groups, *e.g.*, -OH, $-CO_2H$, $-NH_2$, forms a primary valence bond with the central metal atom by elimination of a proton.

In most structure studies of azo dye lakes the azo group has been found to fill only one coordination position of a central metal atom, although the azo group contains two nitrogen atoms and an unsaturated bond, *i.e.*, three possible sources of coordination. Azo-methine dyes contain one carbon atom and one nitrogen atom joined by an unsaturated bond in the chromophoric group but form lakes similar to those of azo dyes. Compared to nitrogen atoms, carbon atoms are considered to have negligible coordinating ability, but coordination compounds in which an olefinic linkage is responsible for the addition of an organic molecule to a metal atom are well known (2). Therefore the present investigation was carried out with *ortho-* substituted stilbene compounds to determine whether the nitrogen atom or the unsaturated bond is the principal source of coordination of the azo-methine and azo groups.

Stilbene compounds have structures similar to azo dyes except that the group linking the two aromatic nuclei is composed of two carbon atoms joined by a double bond rather than two nitrogen atoms joined by a double bond. Because

of the absence of nitrogen atoms, coordination by the linking group in stilbene compounds should result essentially from the unsaturated bond.

All efforts to combine salts of copper, nickel, cobalt, chromium, and zirconium with the high-melting forms of o,o′-dimethoxystilbene, and o,o′-dihydroxystilbene gave no indication of lake formation, although the conditions employed were typical for the formation of lakes by azo dyes. However, a platinum derivative of o,o′-dihydroxystilbene was obtained by heating a mixture of chloroplatinic acid and o,o′-dihydroxystilbene to one atom of platinum suggesting that each organic molecule is attached through at least one hydroxy group, because platinum derivatives of stilbene and other simple olefinic compounds have been found to contain only one unsaturated molecule per metal atom (3).

It is concluded that the coordination bond between the azo group and the metal atom in azo lakes is principally the result of the electron pairs on one or both of the nitrogen atoms. The relative contribution of the unsaturated linkage to the strength of the coordination bond must be very slight.

In the course of this study a number of compounds were prepared from aromatic azo compounds and metal halides under anhydrous conditions. Both zirconium tetrachloride and chloroplatinic acid formed compounds with benzeneazo-β-naphthol in which the dye to metal ratio was 2:1. In addition, chloroplatinic acid formed a similar compound with azobenzene. All of these compounds are hydrolyzed readily by water, releasing the original dye and a solution of the metal chloride. The properties and manner of formation are strikingly similar to those of compounds prepared by Fischer and Taurinsch (4), Dermer and Fernelius (5), Kharasch and Ashford (6), and Fricke and Ruschhaupt (7). The compound prepared from chloroplatinic acid and azobenzene serves as a link between the work of Fricke and Ruschhaupt on acid amides and the work of the other authors on azo compounds. Consistent correlation concerning the

structures of all of these compounds is obtained by assuming that the binding force between the organic molecule and the acid or metal halide is a type of hydrogen bond.

Part II. The Tendencies of Various Metallic Elements to Form Lakes with Azo Dyes

Because lakes of azo dyes are coordination compounds, the formation of these lakes should extend to metallic elements other than the readily available elements used in the dye industry. A survey of the lake-forming properties of the various metallic elements shows that the tendency toward the formation of stable azo dye lakes is greatest among the transition elements of Group VIII in the periodic table of elements and does extend to elements beyond period three of the table.

In support of this observation, platinum lakes were prepared from chloroplatinic acid with o,o′-dihydroxyazobenzene and with benzeneazo-β-naphthol. Each of these lakes was produced in a glacial acetic acid medium at a relatively slow rate (twelve to twenty-four hours) by a step-wise reaction, the first principal intermediate being the hydrogen bonded type of compound discussed in Part I. The final products of approximately twenty-four hours of heating were extremely black insoluble precipitates. Analyses of these final products indicate that the chlorine atoms surrounding the platinum atom have not been replaced completely by dye molecules. With benzeneazo-β-naphthol the formula $Pt(dye\text{-}H)_2 . Pt(dye\text{-}H)Cl . H_2O . \frac{1}{2} HCl$ is proposed in which platinum has been reduced to the divalent state. With o,o′-dihydroxyazobenzene the tetravalent state of platinum appears to be stabilized by coordination in the formula proposed, $2Pt(dye\text{-}2H)_2 . PtCl_4$.

Zirconium oxychloride was found not to form stable lakes with mono-ortho-hydroxyazo dyes. However, with o,o′-dihydroxyazobenzene a lake was formed which was soluble in alcohol, ether, and benzene. The formula appears to be

ZrO(dye-2H) . ½ Dye. A possible method of lake formation by dissolving zirconium oxychloride in the molten dye was found to give products having the properties of impure lakes.

Studies with aqueous-alcoholic solutions of beryllium chloride of varying pH gave no indication of lake formation with o,o′-dihydroxyazobenzene.

The trend toward better lake-forming properties among the elements located in or near Group VIII of the periodic table is apparent from the above studies. The platinum ion exhibits its superiority in forming very stable and insoluble lakes with both *mono-* and *di-* orthohydroxyazo dyes, while the zirconyl ion forms lakes with dihydroxyazo dyes but not with monohydroxyazo dyes. Finally, the beryllium ion, small in radius and deficient in available bonding orbitals gives no indication of forming lakes even with di-orthohydroxyazo dyes.

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VITA

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